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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003900404 for a patent by UNIVERSITY OF WOLLONGONG and MASSEY UNIVERSITY as filed on 31 January 2003.

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Twelfth day of February 2004

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES



AUSTRALIA

PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:-

"CONDUCTING POLYMERS WITH PORPHYRIN CROSS-LINKERS"

The invention is described in the following statement

TECHNICAL FIELD

The present invention relates to conductive electrofunctional polymers, methods of synthesising such electrofunctional polymers, and the use of such polymers.

BACKGROUND ART

5 Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

10 Porphyrins are interesting molecular structures which provide the basis of the light harvesting capabilities of chlorophyll and the oxygen binding capabilities of heme in addition to possessing electron transfer mediation capabilities.

15 Procedures that enable porphyrin groups to be immobilised on polymeric backbones are known. This may be achieved either by forming copolymers with other vinyl monomers, covalently binding porphyrins to preformed polymers, or by polymerising groups (vinyl) attached to a natural or synthetic porphyrin. A particularly interesting process involves attachment of electropolymerisable groups to porphyrins, which can then be used to form a thin coating of the polymeric material on electrodes such as platinum or ITO glass. The synthesis and application of porphyrin containing polymers has been reviewed (Bao, Z.; Yu, L. Trends in Polymer Science, 1995, 3, 159 and references cited therein). Using porphyrin-containing monomers, insoluble films can be electrodeposited 20 and used for a range of applications, including electrocatalysis, as chemical and biosensors, or in solar energy conversion. Sulfonated porphyrins have been incorporated as counter ions into conducting polymer structures. Porphyrins have also simply been added to conducting polymer mixtures.

25 One of the limitations possessed by previous porphyrin-containing polymers and polymerisable monomers has been that the large porphyrin moiety has significantly disrupted electronic communication within the polymer, reflected in the poor conductivity of the porphyrin-polymer films. In addition, the integration of the porphyrin into the polymer chain has frequently changed the characteristics of the polymer for which it was chosen. The attachment of two monomer molecules to the porphyrin and subsequent homo- 30 or copolymerisation has the potential to afford cross-linked polymers in which the characteristics of both the polymer and the porphyrin are retained.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

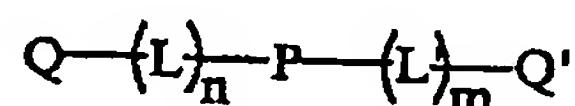
SUMMARY OF THE INVENTION

The present invention describes for the first time in one preferred embodiment a 5 molecule comprising a porphyrin moiety, two or more thiophenes or related heterocyclic systems, and a means of forming polymers with good porphyrin/polymer chain communication and less steric disruption of the polymer chains. The invention also describes synthetic methods for preparing monomeric precursor units and corresponding functionalised polymers.

10 Throughout this specification the term "electrofunctional" is taken to refer to groups, which are adapted to donate or accept electrons, or possess inherent photovoltaic or chemical transport properties.

According to a first aspect, the invention consists in a cross-linking monomer unit having the structure:

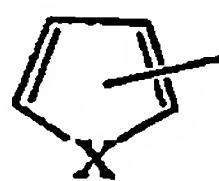
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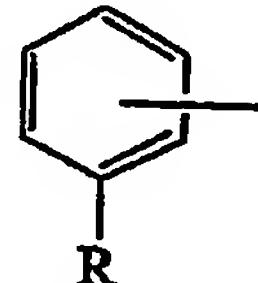
where Q and Q' are polymerisable units, P is an electrofunctional unit and L and L' are linkers providing direct or indirect electronic communication between P and Q and Q', and wherein n = 0, 1, 2 or 3 and m = 0, 1, 2 or 3.

Preferably Q and Q' are heteroaromatic rings of the general formula

20



and

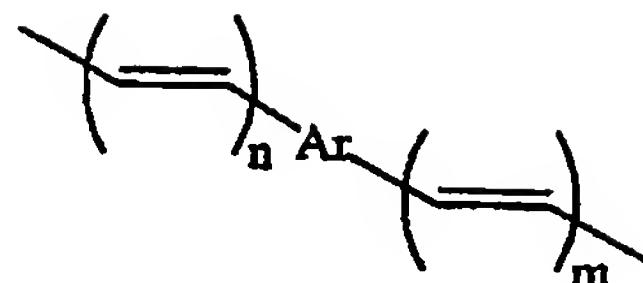


where R can be any suitable polymerisable or non-polymerisable functional group and X can be selected from S, NH or O. Suitable heteroaromatics include: thiophene, substituted 25 thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

Preferably the linkers L and L' are selected from the group comprising:



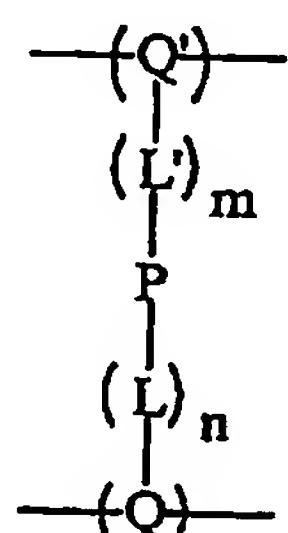
and



wherein $n = 0, 1, 2$ or 3 , $m = 0, 1, 2$ or 3 , and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

Preferably P is selected from the group comprising: porphyrin, substituted porphyrin, phthalocyanine, substituted phthalocyanine or other tetranitrogen-containing macrocycle. These groups may or may not be coordinated to metals.

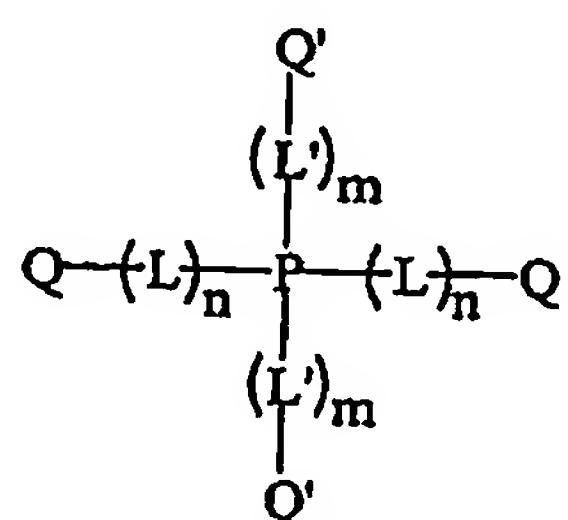
According to a second aspect, the invention consists in a polymer having the 10 structure:



where P is an electrofunctional unit, Q and Q' are polymerisable units, L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q' , and wherein $n = 0, 1, 2$ or 3 and $m = 0, 1, 2$ or 3 .

15 The preferences of Q and Q' , L and L' , and P are the same as the preferences for the first aspect.

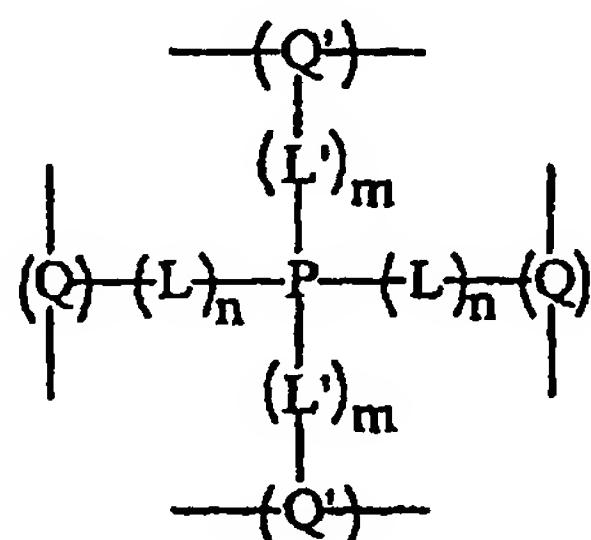
According to a third aspect, the invention consists in a cross-linking monomer unit having the structure:



where P is an electrofunctional unit, Q and Q' are polymerisable units, and L and L' are linkers providing direct or indirect electronic communication between Q and Q', and wherein n = 0, 1, 2 or 3 and m = 0, 1, 2 or 3.

The preferences of Q and Q', L and L', and P are the same as the preferences for 5 the first aspect.

According to a fourth aspect, the invention consists in a polymer having the structure:



where P is an electrofunctional unit, Q and Q' are polymerisable units, L and L' are 10 linkers providing direct or indirect electronic communication between Q and P and between P and Q', and wherein n = 0, 1, 2 or 3 and m = 0, 1, 2 or 3.

The preferences of Q and Q', L and L', and P are the same as the preferences for the first aspect.

According to a fifth aspect, the invention consists in a copolymer comprising a 15 monomer according to the first aspect and one or more members of the group comprised of: benzene, substituted benzene, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

According to a sixth aspect, the invention consists in a copolymer comprising a cross-linking monomer unit according to the third aspect.

20 According to a seventh aspect, the invention consists in a monomer, polymer, cross-linking monomer unit or copolymer according to any one of the previous aspects further comprising a solubilising group. A preferred solubilising group is SO_3^- .

According to an eighth aspect, the invention consists in an electrofunctional material including a base material and a polymer or copolymer according to the second 25 aspect or any one of the fourth to seventh aspects. Preferably the electrofunctional material is a photovoltaic, electrocatalytic or corrosion inhibiting material. Preferably the base material is textile, glass or metal.

According to a ninth aspect, the invention consists in an electrofunctional material including a base material and a copolymer according to the fifth aspect. Preferably the electrofunctional material is a photovoltaic, electrocatalytic or corrosion inhibiting material. Preferably the base material is textile, glass or metal.

5. According to a tenth aspect, the invention consists in a method of preparing a monomer according to the first aspect, said method comprising the step of reacting a thiophenecarboxaldehyde with a dipyrromethane compound.

According to an eleventh aspect, the invention consists in a method of forming a polymer comprising the steps of polymerising a cross-linking monomer according to the 10 first or third aspects. The polymerisation may be carried out by oxidation, which may be chemical or electrochemical.

According to a twelfth aspect, the invention consists in a method of preparing an electrofunctional material comprising the steps of contacting a base material with a cross-linking monomer according to the first or third aspects and subsequently polymerising the 15 monomer.

According to an thirteenth aspect, the invention consists in a method of preparing an electrofunctional material according to the twelfth aspect further including the step of adding to the monomer one or more members of the group comprised of benzene, thiophene, furan or pyrrole. benzene, substituted benzene, aniline, substituted aniline, 20 thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

The invention further consists in a method of corrosion inhibition comprising the step of adding a polymer or copolymer according to any one of the second or fourth to seventh aspects to a surface in need of such corrosion inhibition.

25 The invention further consists in a method of corrosion inhibition comprising the step of adding one or more components selected from the group comprising a cross-linking monomer of the first or third aspects to a surface in need of such corrosion inhibition and polymerising such units in-situ, optionally in the presence of another monomer, polymer or copolymer. Suitable other monomers include benzene, substituted benzene, aniline, 30 substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

The invention further consists in a method of light harvesting comprising the steps of adding a polymer or copolymer according to any one of the second or fourth to seventh aspects to a surface, applying light to the resultant surface, or exposing said surface to light, and capturing the resultant current.

5 The invention further consists in a method of light harvesting comprising the steps of adding one or more components selected from the group comprising a monomer of the cross-linking monomer of the first or third aspects to a surface, polymerising such units in-situ, optionally in the presence of another monomer, polymer or copolymer, applying light to the resultant surface, or exposing said surface to light, and capturing the resultant
10 current. Suitable other monomers include benzene, substituted benzene, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

15 The invention further consists in a method of electrocatalysis comprising the steps of adding a polymer or copolymer according to any one of the second or fourth to seventh aspects to a surface, contacting the resultant surface with a reaction mixture requiring electrocatalysis and applying a current.

20 The invention further consists in a method of electrocatalysis comprising the steps of adding one or more components selected from the group comprising a cross-linking monomer of the first or third aspects to a surface, polymerising such units in-situ, optionally in the presence of another monomer, polymer or copolymer, contacting the resultant surface with a reaction mixture requiring electrocatalysis and applying a current. Suitable other monomers include benzene, substituted benzene, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

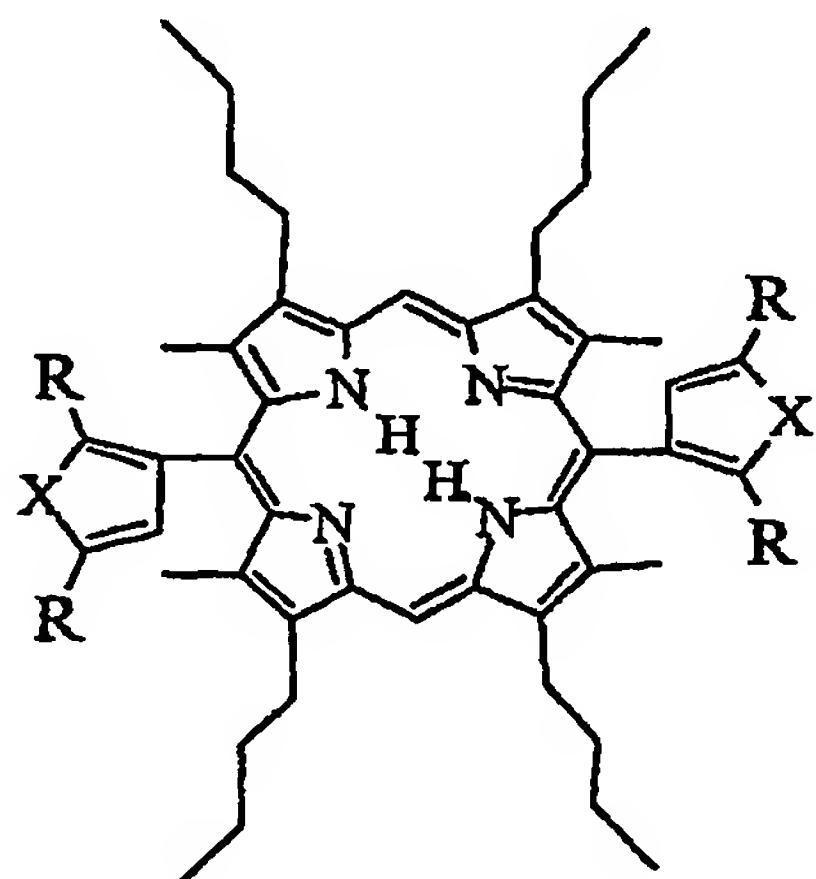
25 Further embodiments of the invention are also envisaged which include the addition of components which exhibit electrochromism, thermochromism, optical activity, metal chelation, molecular recognition, chemical sensing, high anodic stability and liquid crystalline effects and also functionalities suitable for subsequent chemical derivatisation, for instance, to attach enzymes or other biological entities.

30 Unless the context clearly requires otherwise, throughout the description and the claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive

sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

DESCRIPTION OF PREFERRED EMBODIMENT

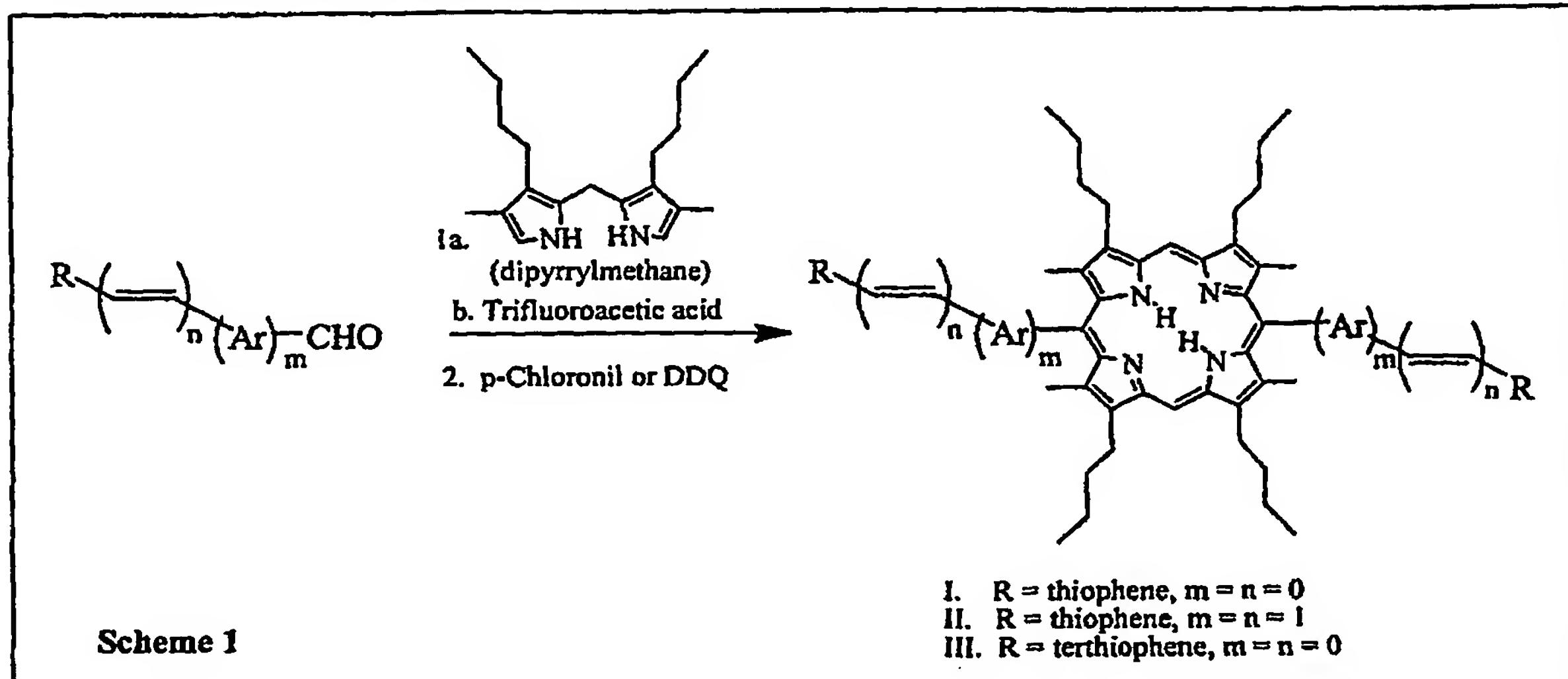
Organic synthesis procedures and polymerisation protocols have been developed
5 which allow the preparation of novel compounds in accordance with the invention having a
porphyrin cross-linked via conjugated chains or aromatic groups to conducting polymer
backbones. Such a structure enables interaction between the porphyrin moiety and the
conducting polymer with significantly reduced disruption of the polymer backbone. This
results in enhanced photovoltaic and electron transfer compared to other porphyrin-
10 containing structures and provides conducting polymers sensitive to chemicals capable of
binding to the porphyrin or other tetrapyrrolic macrocycle.



$X = S, NH$ or O
 $R = H, aryl$ or $heteroaryl$

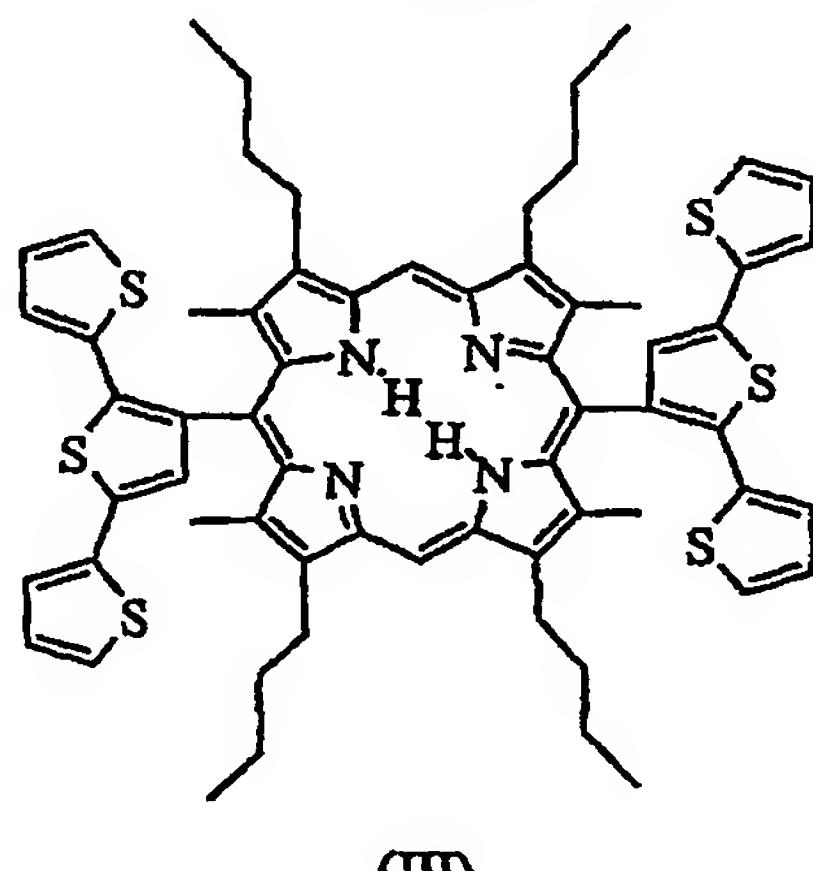
Monomeric units of the invention having thiophene ($X = S$, $R = H$) or terthiophene ($X = S$, $R = \text{thiophene}$). A preferred structure is shown above. Electrochemical or 15 chemical polymerisation of these monomeric units results in the aforementioned porphyrin cross-linked to a conducting polymer backbone. The polymer product exhibits good photovoltaic performance due to the ability of the porphyrin moiety to harvest light and pass a hole to the conducting polymer backbone. The polymer product also possesses enhanced electrocatalytic performance and is useful as an active component for corrosion 20 inhibition.

A synthetic methodology, illustrated in Scheme 1 has been developed which allows the synthesis of a wide variety of heteroaromatic porphyrin monomer crosslinkers in accordance with the invention. Specifically I - III have been synthesised.



5

The terthiophene derivative (III) electrochemically polymerises to form a blue film, the CV of which is consistent with a conducting polymer.



(III)

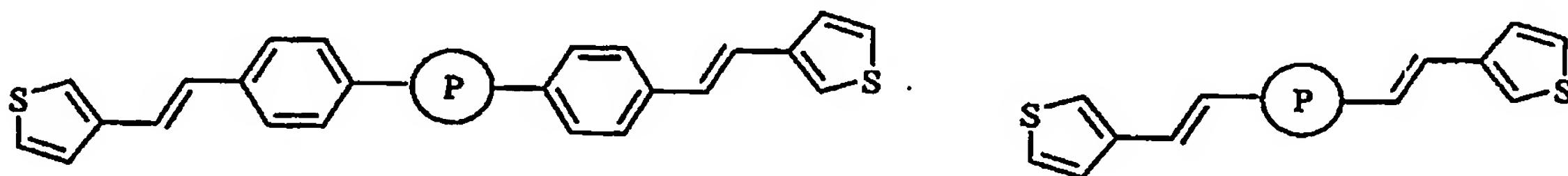
10 Notwithstanding this, these materials are of greater interest as crosslinkers in copolymers. Thus, copolymers containing (III) and terthiophene (1:2 ratio confirmed using elemental analysis) have been produced. The polymers are electrofunctional and exhibit the UV-vis spectra expected for a conducting polymer. This permits copolymerisation of 15 this porphyrin terthiophene not only with other thiophenes but also with pyrrole and its derivatives. Similar chemistry can also occur with porphyrin thiophenes (I and II). Thus

these materials are extremely valuable as active crosslinkers for electrofunctional polymers and copolymers.

One of the great advantages of using the porphyrin moiety is the ability to 'tune' the electronic state of the porphyrin by insertion of appropriate metal atoms. Thus the copper and zinc derivatives, (Cu-III) and (Zn-III), have been prepared and shown to act as copolymer cross-linkers with terthiophene in the manner indicated above.

10 Polymerisation by the electrochemical route is preferred as it provides more accurate in-situ control of the energy injected into the polymerisation reaction. It has been demonstrated for polypyrroles and polyanilines that this can be used to advantage in manipulating and improving the properties of the resultant material.

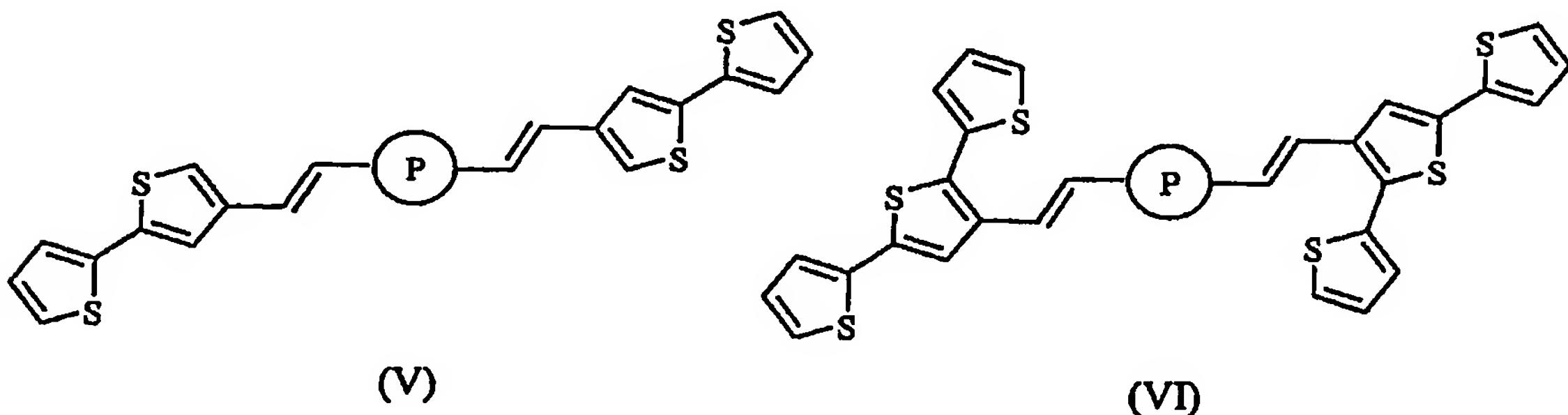
A variety of porphyrin derivatives in accordance with the invention can be made utilising the chemistry and compounds outlined in Scheme 1. Thus, an extended porphyrin-thiophene monomer (II) can be made, as can the shorter porphyrin-thiophene cross linker (IV) by extension of the thiophene aldehyde.

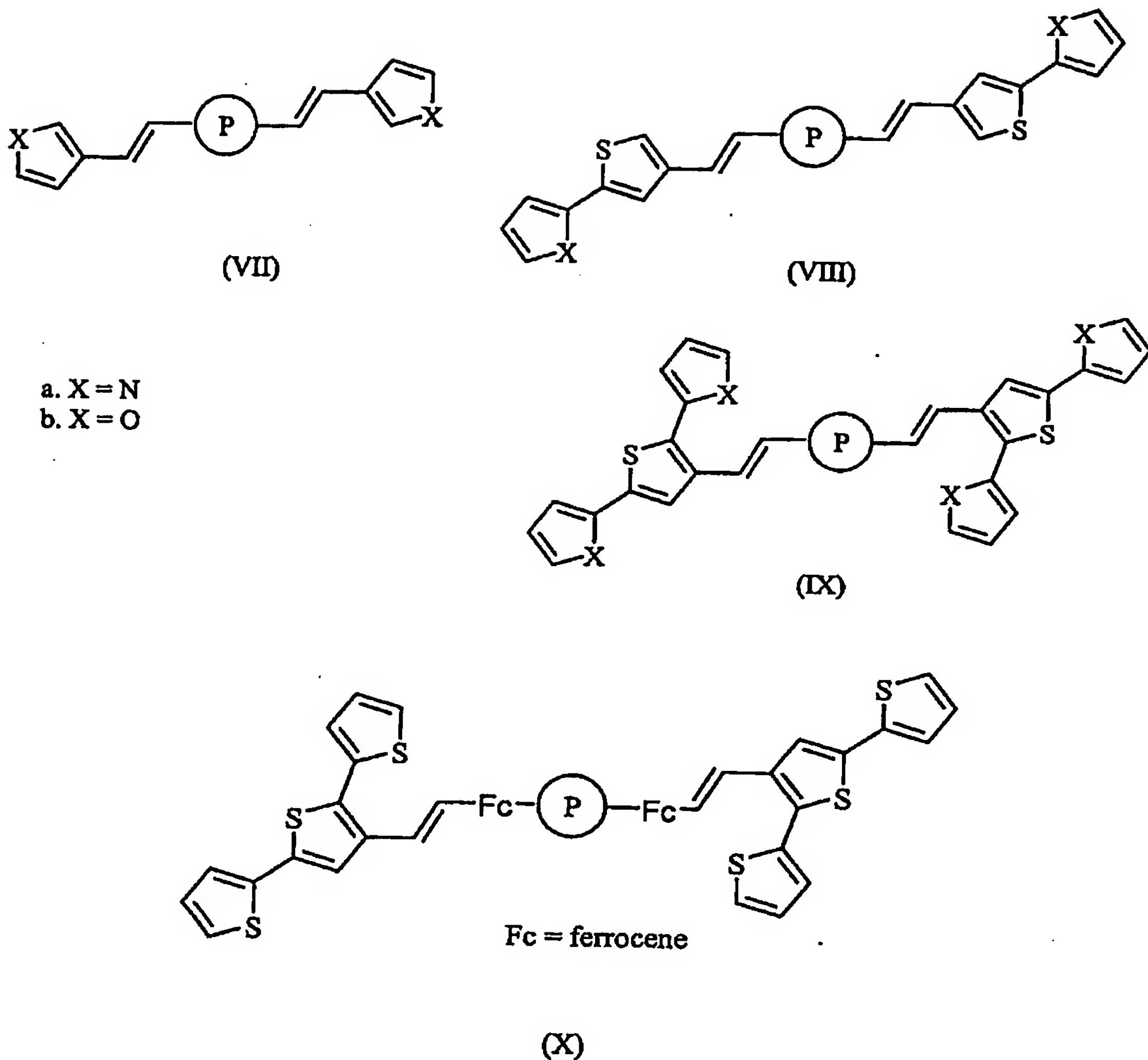


(II) P = porphyrin

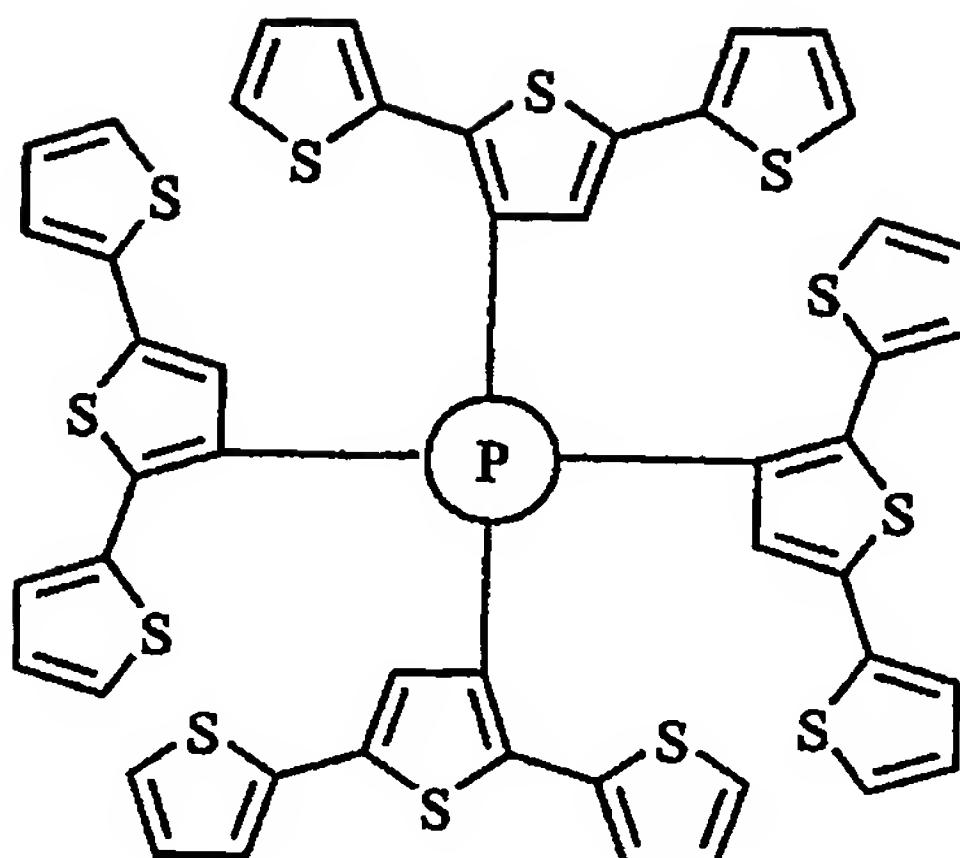
(IV)

Identically substituted bithiophenes, terthiophenes and oligomers can also be made using this chemistry. Thus, bithiophene (V) and terthiophene (VI) are readily available from the corresponding aldehydes. The pyrrole or furan derivatives (VIIa,b), (VIIIa,b) and 20 (IX) can similarly be prepared.





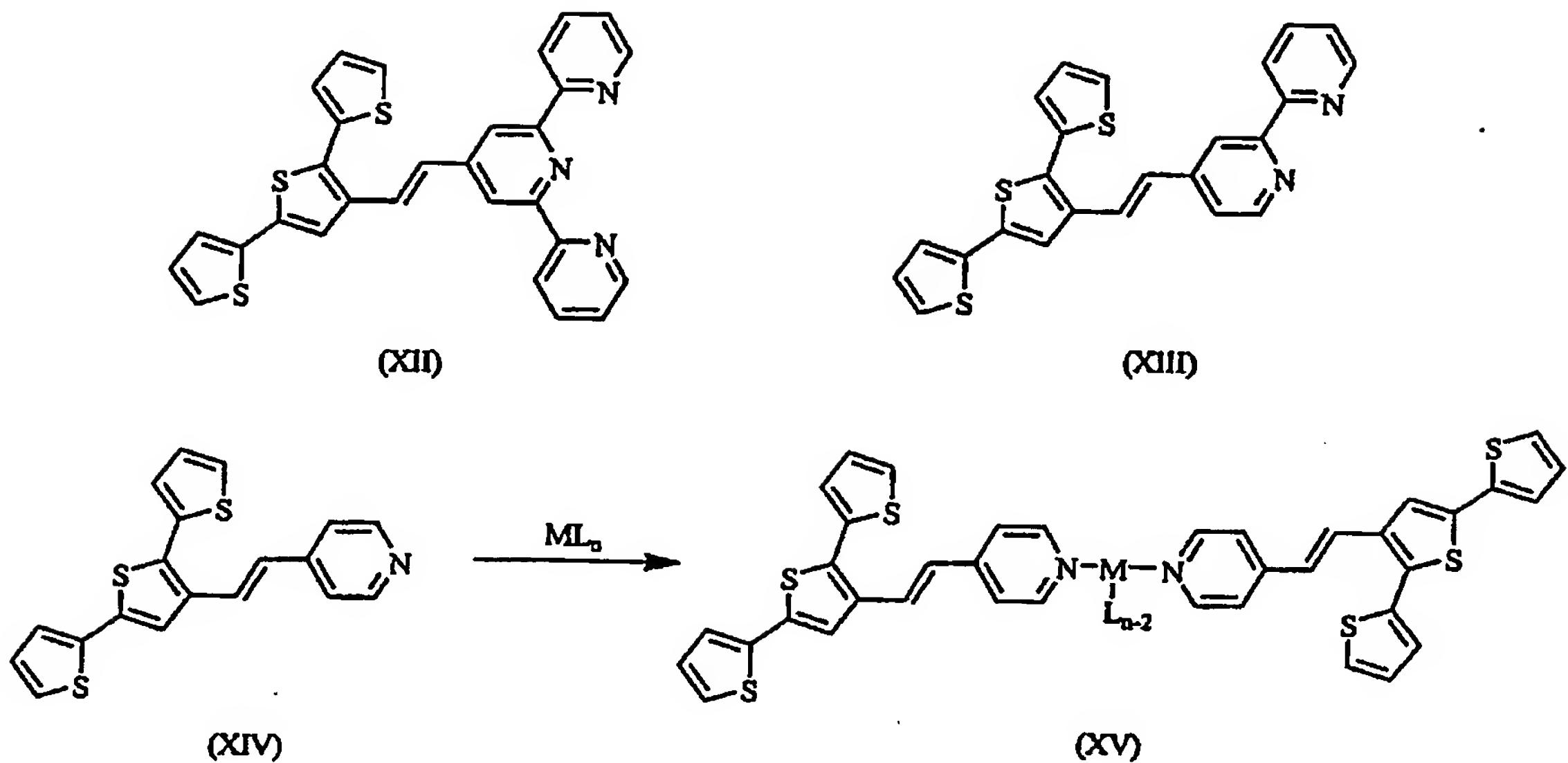
5 The aromatic rings in products such as (II) can be replaced with a variety of other useful derivatives such as ferrocene. Thus, the bisterthiophene-ferrocene-porphyrin (X) can be readily prepared from the appropriate terthiophene-ferrocene aldehyde using the procedure outlined in Scheme 1. This provides a way to introduce redox-active functionality into cross-linkers, in close proximity to the porphyrin moiety.



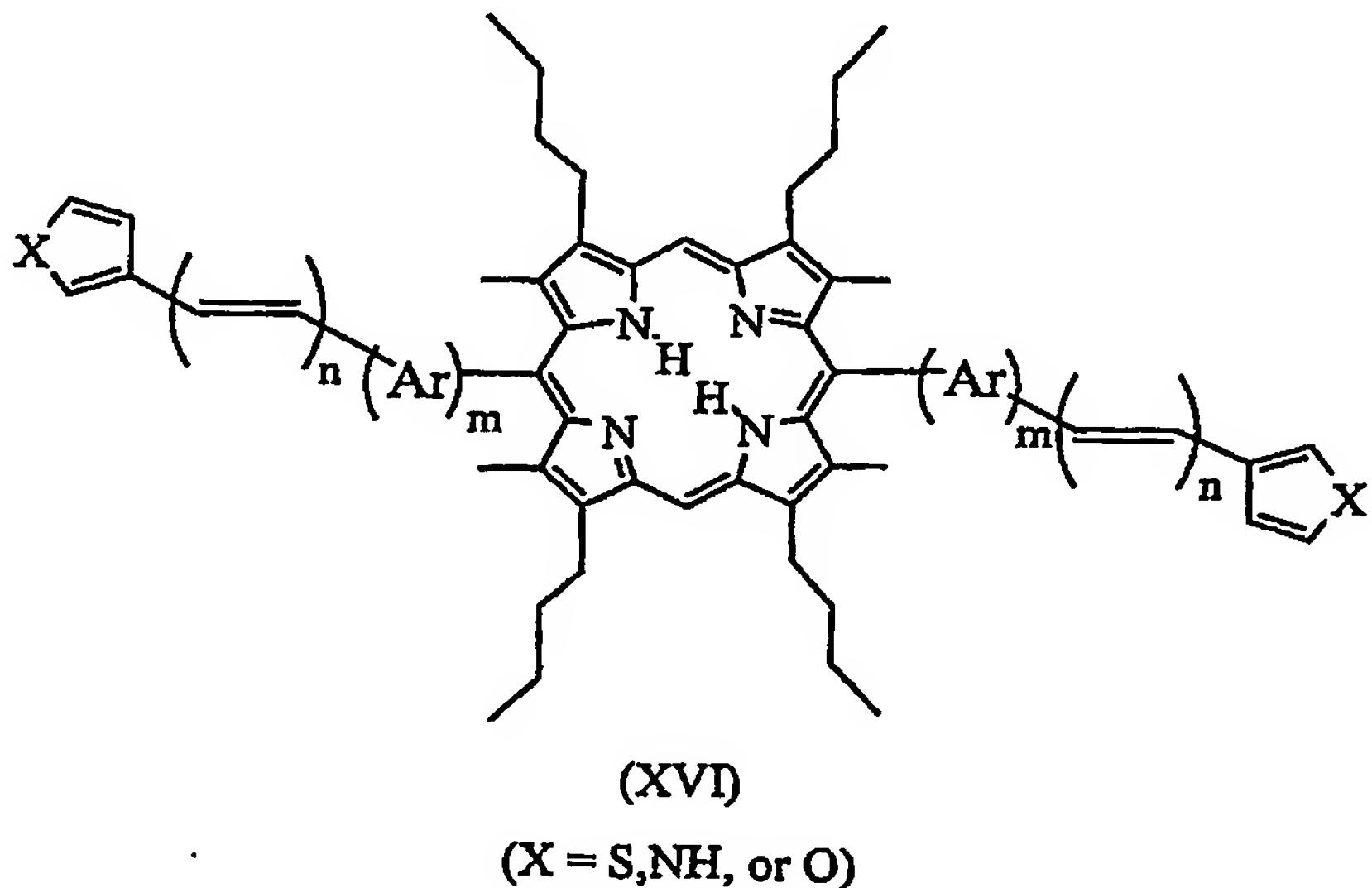
(XI)

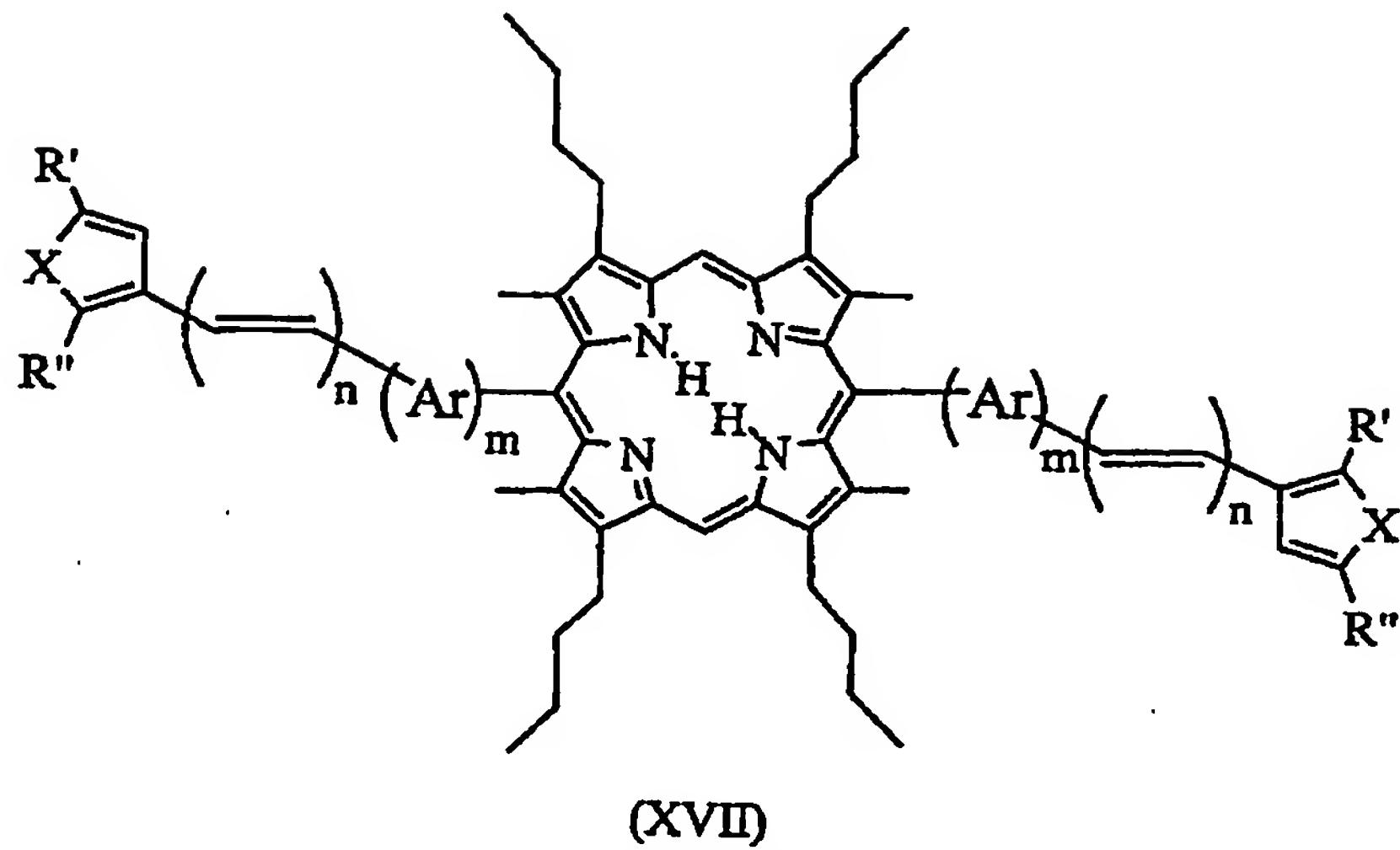
Replacing the dipyrromethane reactant in Scheme 1 with pyrrole provides a way to make tetrasubstituted porphyrin cross-linkers. The tetraterthiopheneporphyrin (XI) has 5 been easily prepared this way and shown to undergo electrochemical polymerisation to give blue conducting polymer films.

Other photoactive functionalities can be exploited using this approach. For example, polypyridine functionalised terthiophenes (XII - XIV) are obtained from the reaction of terthiophene methylphosphonate with pyridine, bipyridine, or terpyridine 10 aldehydes (Collis, G. E., Burrell, A. K., and Officer, D. L., *Tetrahedron Letters*, 2001, 42, 8733-8735). Complexation of these monomers with suitable metal ligand derivatives provides bisterthiophene metal complex monomer cross-linkers such as (XV). These monomers have the potential to provide light harvesting cross-linked conducting polymers, analogous to the porphyrin terthiophenes.



While the preferred embodiments herein are described in terms of thiophene-based monomers, a person skilled in the art will appreciate all this chemistry is applicable to other heteroaromatic derivatives such as pyrrole and furan. For example, the 5 heteroaromatic-porphyrin monomers (XVI) can be prepared and polymerised with thiophene, pyrrole and furan. Thus, oligomers such as (XVII) are available using the described methodologies.

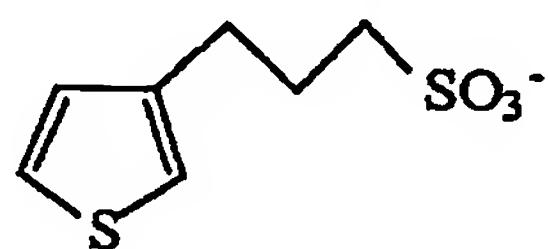




(XVII)

(X = S, NH, or O; R' = oligothiophene, oligopyrrole or oligofuran; R'' = oligothiophene, oligopyrrole or oligofuran)

5 Many of the applications of the conducting polymers with porphyrin groups attached in electronic communication benefit from production of polymers in "soluble" form. Such materials of the invention are then more amenable to subsequent processing as coatings or for device fabrication. Electro-hydrodynamic processing methods allow either colloids or truly soluble polymers to be produced if desired. These processing methods can
10 be used in the production of colloidal forms, nanoparticles or nanofibres of the polymers of the invention. Alternatively soluble forms of the photoactive polymers can be prepared by forming copolymers with monomers such as (XVIII),



(XVIII)

15 or by using polyelectrolytes as counterions to induce solubility.

A preferred application of the polymers of the invention is in the production of photovoltaic materials, and in particular textiles. Chemical polymerisation directly onto substrates is achieved by dipping the substrate in a monomer of the invention followed by exposure to an oxidant. This process is applicable to either conductive or non conductive
20 substrates including cloths, glass, or other structural materials.

A preferred embodiment will now be described with reference to the following examples.

EXAMPLES

In the Examples, ^1H nuclear magnetic resonance (NMR) spectra were obtained at 270.19 MHz using a JEOL JMN-GX270 FT-NMR Spectrometer with Tecmag Libra upgrade, and at 400.132 MHz using Bruker 400 Avance running X-WIN-NMR software.

5 The chemical shifts are relative to TMS or to the residual protium in deuterated solvents (CDCl_3 , 7.25 ppm; pyridine-d₅, 7.00, 7.35, 8.50 ppm; DMSO-d₆, 2.50 ppm; MeOD-d₄, 3.35 ppm) when TMS is not present. ^{13}C NMR chemical shifts are relative to CDCl_3 (77.0 ppm), pyridine-d₅ (123.4, 135.3, 149.8 ppm), MeOD-d₄, (49.0 ppm). Electronic absorption spectra were obtained using a Shimadzu UV-3101PC UV-VIS-NIR-Scanning

10 Spectrophotometer. Mass spectra were recorded using a Varian VG70-250S double focusing Magnetic sector mass spectrometer. Samples analysed by fast atom bombardment (FAB) high resolution mass spectra (HRMS) were supported in a p-nitrobenzyl alcohol matrix and the data put through VG-OPUS software to give ± 5 ppm error formulations on molecular ions. Major fragmentations are given as percentages relative to the base peak

15 intensity. Chromatography was carried out using Silica (0.032-0.063 mm, Merck Kieselgel 60). Thin layer chromatography was performed using precoated silica plates (Merck Kieselgel 60F₂₅₄).

Chromatography solvents used in the Examples were laboratory grade. Water was purified by reverse osmosis. All other solvents used were AR grade unless otherwise 20 stated. Iodine was sourced from M & B, and was resublimed to >99.8% purity. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was sourced from BDH and was GP grade. 3-Thiophenecarboxaldehyde (98%) was sourced from Aldrich. 3'-Formyl-2,2':5',2"-terthiophene was prepared according to the procedure developed at Massey University (Collis, G. E., Burrell, A. K., and Officer, D. L., Tetrahedron Letters, 2001, 42, 8733-8735). The dipyrromethane was prepared 25 according to the reported procedure (Sessler, J. L., Johnson, M. R., Creager, S. E., Fettinger, J. C. and Ibers, J. A., Journal of the American Chemical Society, 1990, 112, 9310-9329).

The reactions were carried out under an inert atmosphere and shielded from ambient light.

Example 1: Synthesis of 5,15-Bis(3'-thienyl)-2,8,12,18-tetra-n-butyl-3,7,13,17-tetramethylporphine (I).

3-Formylthiophene (30.6 mL, 0.349 mmol) and dipyrromethane (100 mg, 0.349 mmol) were dissolved in degassed anhydrous CH_2Cl_2 (35 mL) at room temperature. Then TFA (26.9 mL, 0.349 mmol, 1.0 equiv.) was added and the solution stirred under N_2 . At the first sign of baseline material by TLC (\approx 15 minutes; silica gel, CH_2Cl_2) the reaction was quenched by the addition of DBU (52.2 mL, 0.349 mmol, 1.0 equiv.). Then *p*-chloranil (214 mg, 0.873 mmol, 2.5 equiv.) was added and the solution stirred for 4 h at room temperature. Next Et_3N (36 mL, 0.258 mmol) was added and reaction stirred vigorously for 1.5 h. Then excess Et_3N (0.723 mL, 5.190 mmol) was added and reaction stirred for 15 min (forms complex with *p*-Chloranil that is soluble in methanol). The product was precipitated out of solution with methanol, filtered and dried under high vacuum to give product (I) (69.3 mg, 53%) as a purple crystalline solid. ^1H NMR (270 MHz) δ -2.41 (br s, 2H, NH), 1.13 (t, 12H, J = 7.3 Hz, CH_2CH_3), 1.78-1.90 (appt sex, 8H, J = 7.6 Hz, CH_2CH_3), 2.13-2.28 (m, 8H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.66 (s, 12H, CH_3), 4.03 (t, 8H, J = 7.6 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.77 (br s, 6H, H thiophene), 10.26 (s, 2H, H 10, H 20). ^{13}C NMR (68.1 MHz) δ 13.7, 14.3, 23.4, 26.5, 35.6, 97.0, 111.7, 124.4, 126.8, 132.6, 136.2, 141.3, 142.0, 143.1, 145.4. UV-vis (CH_2Cl_2): λ_{max} [nm] ($\epsilon \times 10^3$) 408 (210), 507 (20), 542 (9.1), 574 (10), 627 (5.4), 674 (3.7), 725 (3.7). FAB-LRMS: m/z (% assignment) 755 (100%, MH^+). HRMS: Calcd for MH^+ ($\text{C}_{48}\text{H}_{59}\text{N}_4\text{S}_2$): 755.4181, found: 755.4162.

Example 2: Synthesis of 5,15-Bis([2',2'':5'',2'''-terthiophen]-3''-yl)-2,8,12,18-tetra-n-butyl-3,7,13,17-tetramethylporphine (III).

3'-Formyl-2,2':5',2''-terthiophene (96.5 mg, 349 μmol) and dipyrromethane (100 mg, 349 μmol) were dissolved in degassed dry CH_2Cl_2 (35 mL) at RT. TFA (26.9 μL , 349 μmol , 1.0 eq) was added and the solution stirred under N_2 . At the first sign of baseline material by TLC (\approx 15 minutes; silica gel, CH_2Cl_2) the reaction was quenched by the adding DBU (52.2 μL 349 μmol , 1:0 eq). Then *p*-chloranil (214.5 mg, 873 μmol , 2.5 eq) was added and the solution stirred for 4 h at RT. Next Et_3N (36 μL , 258 μmol) was added and reaction stirred vigorously for 1 h. Excess Et_3N (723 μL , 5.190 mmol) was added and reaction stirred for 15 min. The product was then precipitated out of solution with MeOH, to give

product (III) (76.9 mg, 41%) as a brownish-purple solid. ^1H NMR (400 MHz, CDCl_3 , TMS): δ -2.309 (br d, 4H, [-2.304 ($\text{NH}_{(\alpha\alpha \text{ or } \alpha\beta)}$), -2.314 ($\text{NH}_{(\alpha\beta \text{ or } \alpha\alpha)}$)]), 1.067 (t, 24H, $^3J = 7.3$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.65-1.78 (app sext, 16H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.11-2.26 (app pent, 16H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.898 (s, 24H, $\text{H}_{\text{Me-TBMP}}$), 3.90-4.10 (m, 16H, 5 $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6.40-6.48 (m, 8H, $\text{H}_{4''}$, 5', thietyl A), 6.753 (dd, 2H, $^3J = 3.4$, $^4J = 1.5$ Hz, $\text{H}_{3''}$ ($\alpha\beta$ or $\alpha\alpha$), thietyl A), 6.786 (dd, 2H, $^3J = 3.4$, $^4J = 1.5$ Hz, $\text{H}_{3''}$ ($\alpha\alpha$ or $\alpha\beta$), thietyl A), 7.12-7.15 (4H, [7.129 (dd, $^3J = 5.1$, 3.6 Hz, $\text{H}_{4''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.136 (dd, $^3J = 5.1$, 3.6 Hz, $\text{H}_{4''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl C}}$), 7.29-7.31 [4H, [7.294 (dd, $^3J = 5.2$ Hz, $^4J = 1.1$ Hz, $\text{H}_{5''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.304 (dd, $^3J = 5.2$ Hz, $^4J = 1.1$ Hz, $\text{H}_{5''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl C}}$), 7.44-7.46 (4H, [7.448 (dd, $^3J = 3.7$ Hz, $^4J = 1.1$ Hz, 10 $\text{H}_{3''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.458 (dd, $^3J = 3.7$ Hz, $^4J = 1.1$ Hz, $\text{H}_{3''}$ ($\alpha\beta$ or $\alpha\alpha$)), $\text{H}_{\text{thietyl C}}$], 7.630 (app d, 4H, [7.629 ($\text{H}_{4''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.631 ($\text{H}_{4''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl B}}$), 10.227 (app d, 4H, [10.224 ($\text{H}_{10, 20}$ ($\alpha\alpha$ or $\alpha\beta$)), 10.230 ($\text{H}_{10, 20}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{meso}})$. Assignments aided by COSY spectra. ^{13}C NMR (101 MHz): δ 13.71, 13.72, 14.2, 23.3, 26.5, 35.6, 97.2, 108.6, 110.18, 110.21, 124.1, 124.2, 124.8, 124.9, 125.4, 126.2, 126.3, 128.1, 130.0, 130.1, 134.1, 134.2, 135.4, 135.5, 15 136.0, 136.1, 136.5, 137.2, 138.5, 141.9, 143.5, 145.4, 145.5. UV-vis (CH_2Cl_2): λ_{max} [nm] ($\epsilon \times 10^{-3}$) 415 (203), 511 (17.8), 546 (7.06), 577 (7.59), 630 (3.23). FAB-LRMS: m/z (% assignment) 1083 (100, MH^+). HRMS: Calcd for MH^+ ($\text{C}_{64}\text{H}_{67}\text{N}_4\text{S}_6$): 1083.3690, found: 1083.3719.

Example 3: Synthesis of 5,15-Bis([2',2'':5'',2'''-terthiophen]-3''-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato zinc(II) (Zn-III).

20 A solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (42.9 mg, 196 μmol , 1.2 eq) in MeOH (1.0 mL) was added to a solution of bisterthiophenylporphyrin (II) (177 mg, 163 μmol) in CHCl_3 (18 mL) with stirring at RT. The reaction was deemed complete by TLC ($R_f = 0.25$, silica, CH_2Cl_2 :hexane (1:2)) after 30 min. The crude product was precipitated with MeOH and 25 the resulting solid was recrystallised from CH_2Cl_2 / MeOH giving (Zn-III) (189 mg, 100%) as a brick-red powder. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.085 (t, 24H, $^3J = 7.3$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.68-1.79 (app sex, 16H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.13-2.21 (app pent, 16H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.915 (s, 24H, $\text{H}_{\text{Me-TBMP}}$), 3.90-4.05 (m, 16H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 6.34-6.44 (m, 8H, $\text{H}_{\text{thietyl A}}$), 6.78-6.80 (m, 4H, $\text{H}_{\text{thietyl A}}$), 7.12-7.15 (4H, [7.135 (dd, $^3J = 5.1$, 3.7 Hz, $\text{H}_{4''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.137 (dd, $^3J = 5.1$, 3.7 Hz, $\text{H}_{4''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl C}}$), 7.28-7.31 [4H, [7.293 (dd, $^3J = 5.3$ Hz, $^4J = 1.2$ Hz, $\text{H}_{5''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.298 (dd, $^3J = 5.3$ Hz, $^4J = 1.2$ Hz, $\text{H}_{5''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl C}}$), 7.630 (app d, 4H, [7.629 ($\text{H}_{4''}$ ($\alpha\alpha$ or $\alpha\beta$)), 7.631 ($\text{H}_{4''}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{thietyl B}}$), 10.227 (app d, 4H, [10.224 ($\text{H}_{10, 20}$ ($\alpha\alpha$ or $\alpha\beta$)), 10.230 ($\text{H}_{10, 20}$ ($\alpha\beta$ or $\alpha\alpha$))], $\text{H}_{\text{meso}})$.

($\alpha\beta$ or $\alpha\alpha$]), H_{thienyl C}], 7.45-7.47 (4H, [7.459 (dd, 3J = 3.6 Hz, 4J = 1.3 Hz, H_{3'''} ($\alpha\alpha$ or $\alpha\beta$)),
7.463 (dd, 3J = 3.6 Hz, 4J = 1.3 Hz, H_{3'''} ($\alpha\beta$ or $\alpha\alpha$)), H_{thienyl C}], 7.674 (s, 2H, H_{4''} ($\alpha\alpha$ or $\alpha\beta$), thienyl
a), 7.696 (s, 2H, H_{4''} ($\alpha\beta$ or $\alpha\alpha$), thienyl B), 10.188 (s, 4H, H_{10, 20, meso}). *Assignments aided by*
COSY spectra. ^{13}C NMR (101 MHz): δ 14.2, 14.3, 23.3, 26.5, 35.6, 97.8, 111.4, 111.5,
5 124.0, 124.1, 124.58, 124.63, 124.7, 125.4, 126.02, 126.09, 128.1, 130.4, 130.5, 133.86,
133.92, 135.5, 135.6, 136.7, 137.4, 137.89, 137.92, 140.1, 143.7, 146.84, 146.86, 148.1.
UV-vis (CH₂Cl₂): λ_{max} [nm] ($\varepsilon \times 10^3$) 353 (63.2), 418 (336), 504 (4.51), 543 (21.6), 581
(13.4). FAB-LRMS: *m/z* (%₀, assignment) cluster at 1143-1151, 1144 (80, M⁺). HRMS:
Calcd for M⁺ (C₆₄H₆₄N₄S₆Zn): 1144.2747, found: 1144.2791.

10 **Example 4: Synthesis of 5,15-Bis([2',2'':5'',2'''-terthiophen]-3''-yl)-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinato copper(II) (Cu-III).**
A solution of Cu(OAc)₂·H₂O (111 mg, 508 μmol , 1.2 eq) in MeOH (10.0 mL) was added
to a refluxing solution of free-base (III) (500 mg, 461 μmol) in CHCl₃ (50 mL) with
stirring under N₂ atmosphere. After 15 h, TLC analysis indicated that all of (III) had been
15 metallated. The solvent was removed *in vacuo* and the residue was column
chromatographed (silica, 37 mm_{dia} x 90 mm, CH₂Cl₂:hexane (1:2)) collecting the major red
coloured band. Recrystallisation from CH₂Cl₂:MeOH gave (Cu-III) (437.5 mg, 83%) as a
purple solid. UV-vis (CH₂Cl₂): λ_{max} [nm] ($\varepsilon \times 10^3$) 414 (379), 536 (22.0), 574 (20.3).
FAB-LRMS: *m/z* (%₀, assignment) cluster at 1142-1149, 1143 (90, M⁺). HRMS: Calcd for
20 M⁺ (C₆₄H₆₄N₄CuS₆): 1143.2751, found: 1143.2753.

Example 5: Synthesis of 5,10,15,20-Tetrakis([2',2'':5'',2'''-terthiophen]-3''-yl)porphine (XI).

3'-Formyl-2,2':5',2''-terthiophene (158 mg, 0.572 mmol) and pyrrole (39.65 μL , 0.572
mmol) were dissolved in degassed anhydrous CH₂Cl₂ (57 mL) under N₂ at room
25 temperature. BF₃·OEt₂ (7.0 μL , 57 μmol , 0.1 eq) was added and the solution stirred in
dark for 2 h. *p*-Chloranil (105 mg, 0.429 mmol, 0.75 eq) was added and the solution
stirred at reflux temperature for 2 hours. Next excess Et₃N was added and the solvent
removed under reduced pressure. The residue was subjected to column chromatography
(80 mm x 37 mm_{dia}, CH₂Cl₂:hexane (1:1)) collecting the first major porphyrin coloured
30 band (R_f = 0.15, CH₂Cl₂:hexane (1:1)). The product was then precipitated out from a
solution of CH₂Cl₂ with MeOH, then filtered and dried under high vacuum to give product

(XI) (62.4 mg, 34 %) as a purple powder containing an inseparable mixture of four isomers by ^1H NMR. ^1H NMR (270 MHz) δ -2.52-2.44 (2H, [-2.47, br s, -2.50, br s] NH), 6.30-6.47 (m, 8H, H thiophene), 6.66-6.79 (m, 4H, H thiophene), 7.06-7.13 (m, 4H, H thiophene), 7.23-7.30 (m, 4H, H thiophene), 7.39-7.46 (m, 4H, H thiophene), 7.76-7.90 (4H [7.77 (s), 7.78 (s), 7.82 (s), 7.84 (s), 7.86 (s), 7.90 (s), H 4"]], 8.93-9.00 (m, 8H, β -pyrrolic). UV-vis (CH_2Cl_2): λ_{max} [nm] ($\epsilon \times 10^{-3}$) 252 (43), 357 (100), 426 (220), 525 (21), 561 (6.4), 596 (7.5), 654 (1.7). LRMS: m/z (% assignment) 1295 (100%, MH^+). HRMS: Calcd for MH^+ ($\text{C}_{68}\text{H}_{39}\text{N}_4\text{S}_{12}$): 1294.9823, found: 1294.9798.

10 **Example 6: Electro-copolymerisation of III with terthiophene**

The cyclic voltammetry and electro-copolymerisation of the most preferred monomeric unit, III prepared in Example 2, with terthiophene are herein described by way of example only. Cyclic voltammetry in dichloromethane, containing 0.1 M tetrabutylammonium perchlorate supporting electrolyte, revealed that co-monomer 15 oxidation commenced at approximately 0.70V vs Ag/Ag $^+$.

This oxidation process modifies the naked Pt surface somewhat as is evidenced by the presence of a crossover in the cyclic voltammogram. This is due to deposition of the oligomeric or polymeric product.

Chronopotentiograms were recorded using a Pt working electrode whilst applying a 20 current density of 0.5mA/cm 2 . On Pt a steady state potential of \approx 0.80V was generated. The fact that this potential did not increase during the polymerisation time indicates that a conductive polymer was deposited.

Chronoamperograms were also recorded using a Pt working electrode whilst applying a constant potential of 0.90V. After the initial transient, the current increased 25 steadily as the conductive polymeric product was deposited on the electrode.

Elemental analysis of the copolymer electrodeposited from an equimolar mixture solution of III and terthiophene indicated that its composition was 1:2:4 of III:terthiophene:perchlorate counter-anion.

Example 7: Photovoltaic performance

The photovoltaic performance of photoelectrochemical cells incorporating our conducting polymers or copolymers has been investigated. One possible embodiment of a photoelectrochemical cell is given in Figure 1.

5

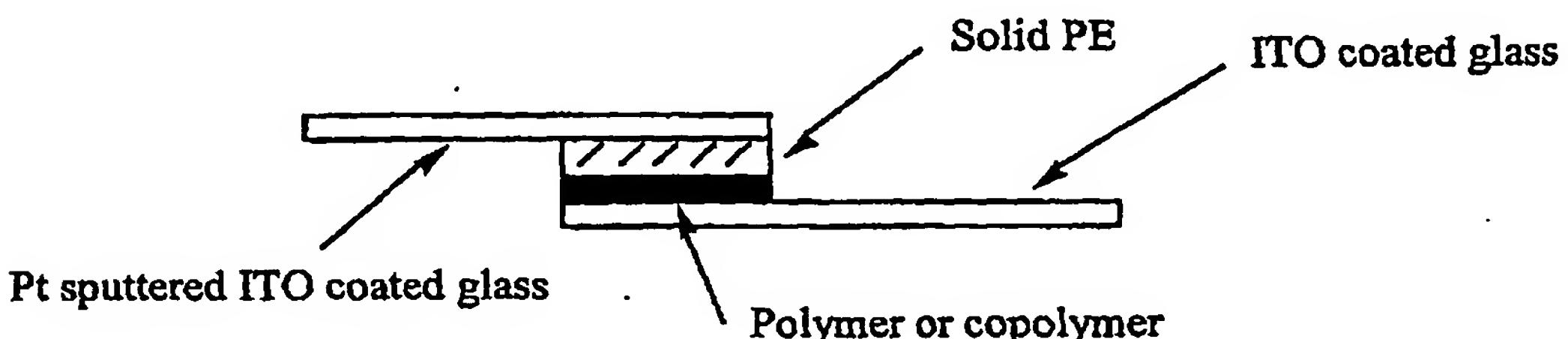


Figure 1. Photoelectrochemical cell

A halogen lamp was used as the white light source and usually an intensity of 500 W/m² was directed at the photoelectrochemical cell. Current-Voltage (I-V) curves were 10 obtained from the photoelectrochemical cell in the dark or in the light by employing Linear Sweep Voltammetry. The I-V curves were then used to determine the Open Circuit Voltage (V_{oc}), the Short Circuit Current (I_{sc}), the Fill Factor, and the Energy Conversion Efficiency (ECE). Some results are shown in Table 1.

15 Table 1. Photovoltaic performance of photoelectrochemical cells incorporating conducting polymers or copolymers.

Type of polymer or copolymer	V _{oc} (mV)	I _{sc} (μ A/cm ²)	Fill Factor	ECE (%)
*Poly(MeTh)	52	1.23	0.24	0.00005
*Poly(BiTh)	247	13.4	0.33	0.0034
**Poly(BiTh)	163	32.1	0.43	0.0071
*Poly(TTh)	187	13.1	0.35	0.0027
**Poly(TTh)	139	123.4	0.38	0.0205
*Poly(TPP-TTh -co-TTh)	185	15.9	0.28	0.0026
**Poly(TPP-	169	27.9	0.35	0.0052

TTh- <i>co</i> -TTh)				
*Poly(TPP-TTh- <i>co</i> -BiTh)	218	4.74	0.30	0.0010
**Poly(TPP-TTh- <i>co</i> -BiTh)	174	17.9	0.32	0.0031
**Poly(BisTTh)	195	229.0	0.38	0.035
**Poly(BisTTh- <i>co</i> -TTh)	212	475.0	0.35	0.069
**Poly(III- <i>co</i> -TTh)	246	581.0	0.31	0.090
**Poly(III- <i>co</i> -TTh) with Zn coordinated	185	881.0	0.36	0.116

Notes. *: solid polymer electrolyte. **: liquid electrolyte

Table 1 shows that the copolymer of III with thiophene (TTh), Poly(III-*co*-TTh), gave the best results and that zinc coordination to the porphyrin moiety enhanced the photovoltaic performance.

5

Although the invention has been described with reference to specific embodiments and examples it will be understood that variations in keeping with the principles and spirit of the invention described are also contemplated and fall within its scope.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A cross-linking monomer having the structure:



where Q and Q' are polymerisable units

5 L and L' are linkers providing direct or indirect electronic communication between P and Q and Q'

P is an electrofunctional unit

wherein n = 0, 1, 2 or 3

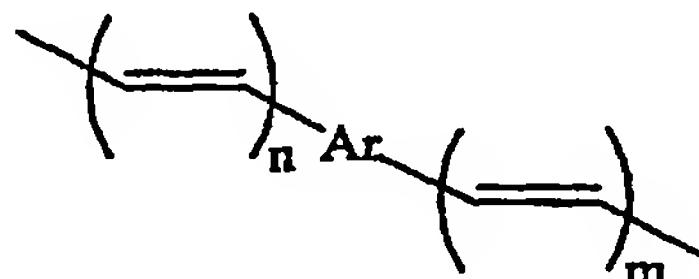
wherein m = 0, 1, 2 or 3

10 2. A cross-linking monomer according to claim 1 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising: substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

3. A cross-linking monomer according to claim 1 or claim 2 wherein L and L' are selected from the group comprising:



and



wherein n = 0, 1, 2 or 3

20 wherein m = 0, 1, 2 or 3

and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

4. A cross-linking monomer according to any one of the preceding claims where P is selected from the group comprising:

25 porphyrin

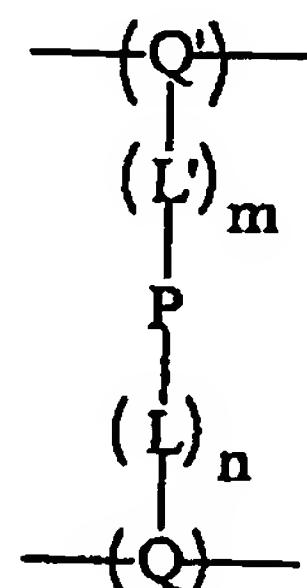
substituted porphyrin

phthalocyanine

substituted phthalocyanine

tetranitrogen-containing macrocycle

5. A cross-linked polymer having the structure:



wherein Q and Q' are polymerisable units

5 L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q'

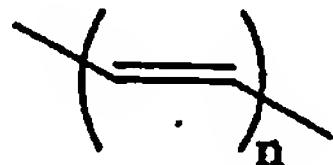
P is an electrofunctional unit

wherein n = 0, 1, 2 or 3

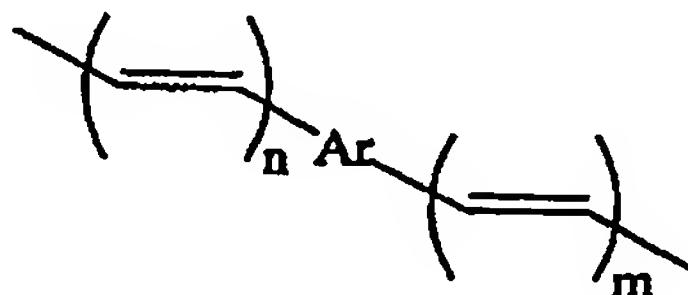
wherein m = 0, 1, 2 or 3

10 6. A cross-linked polymer according to claim 5 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising: substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

7. A cross-linked polymer according to claims 5 or claim 6 wherein L is selected from 15 the group comprising:



and



wherein n = 0, 1, 2 or 3

20 wherein m = 0, 1, 2 or 3

and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

8. A cross-linked polymer according to any one of claims 5 to 7 wherein P is selected from the group comprising:

porphyrin

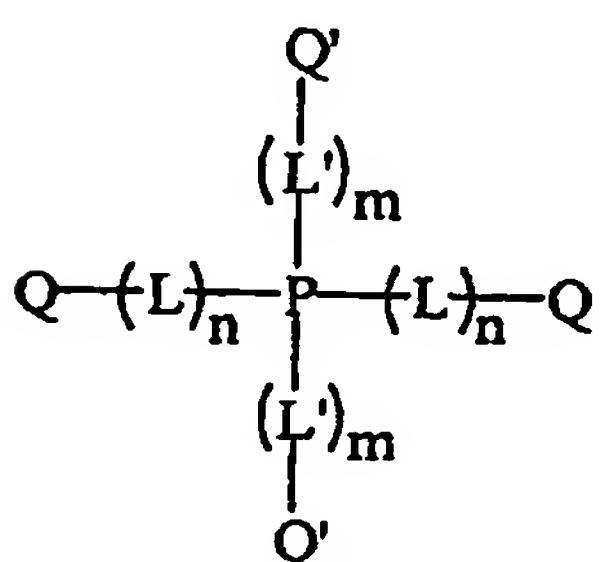
substituted porphyrin

phthalocyanine

substituted phthalocyanine

5 tetranitrogen-containing macrocycle

9. A cross-linking monomer unit having the structure:



wherein:

Q and Q' are polymerisable units

10 L and L' are linkers providing direct or indirect electronic communication between P and Q and Q'

P is an electrofunctional unit

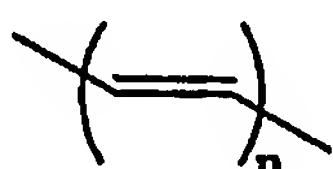
$n = 0, 1, 2$ or 3

$m = 0, 1, 2$ or 3

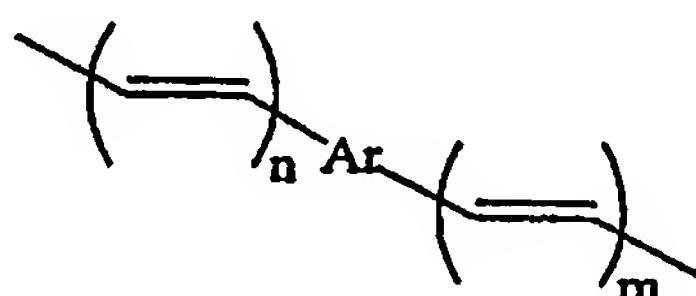
15 10. A cross-linking monomer unit according to claim 9 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising:

substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

20 11. A cross-linking monomer unit according to claim 9 or claim 10 wherein L is
selected from the group comprising:



and



wherein $n = 0, 1, 2$ or 3

wherein $m = 0, 1, 2$ or 3

and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

5 12. A cross-linking monomer according to claim 9 or claim 10 where P is selected from the group comprising:

porphyrin

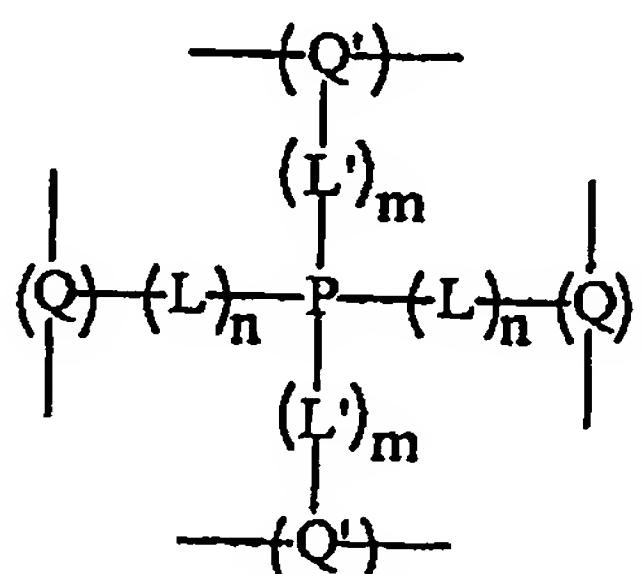
substituted porphyrin

phthalocyanine

10 substituted phthalocyanine

tetrinitrogen-containing macrocycle

13. A cross-linked polymer having the structure:



where Q and Q' are polymerisable units

15 L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q'

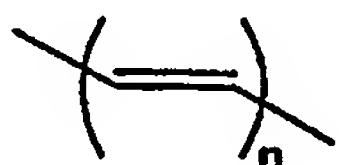
P is an electrofunctional unit

wherein $n = 0, 1, 2$ or 3

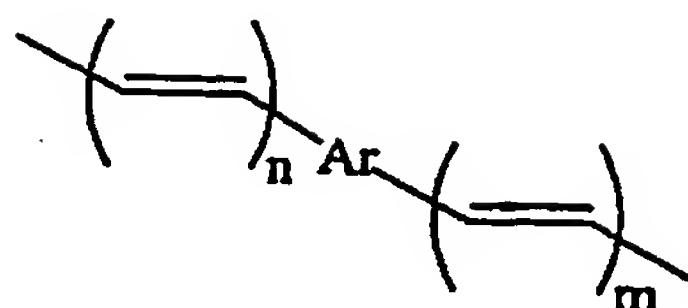
wherein $m = 0, 1, 2$ or 3

20 14. A cross-linked polymer according to claim 13 wherein Q and Q' are substituted aromatic rings or heteroaromatic rings selected from the group comprising: substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

15. A cross-linked polymer according to claims 13 or claim 14 wherein L is selected 25 from the group comprising:



and



wherein $n = 0, 1, 2$ or 3

wherein $m = 0, 1, 2$ or 3

5 and Ar is selected from the group comprising phenyl, naphthyl, polyaryl, heteroaryl, and ferrocenyl or similar metal sandwich complex.

16. A cross-linked polymer according to any one of claims 13 to 15 wherein P is selected from the group comprising:

porphyrin

10 substituted porphyrin

phthalocyanine

substituted phthalocyanine

tetrannitrogen-containing macrocycle

17. A copolymer including a monomer according to any one of claims 1 to 4 and one or

15 more members of the group comprised of substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

18. A copolymer including a monomer according to any one of claims 9 to 12 and one or more members of the group comprised of substituted aromatic, aniline, substituted aniline, thiophene, substituted thiophene, oligothiophene, furan, substituted furan, pyrrole and substituted pyrrole.

19. A monomer, polymer, crosslinking monomer unit or copolymer according to any one of the preceding claims further including a solubilising group.

20. A monomer, polymer, crosslinking unit or copolymer according to claim 19
25 wherein the solubilising group includes a SO_3^- moiety.

21. An electrofunctional material including a base material and a polymer according to any one of claims 5 to 8 or 13 to 16.

22. An electrofunctional material including a base material and a copolymer according to any one of claims 17 to 20.

23. A method of preparing an electrofunctional material comprising the steps of treating a base material with a monomer according to any one of claims 1 to 4 and subsequently oxidising the monomer.
24. A method of preparing an electrofunctional material according to claims 22 or 23 further including the step of adding to the monomeric unit one or more members of the group comprised of thiophene, furan and pyrrole.

5 DATED this 31st day of January 2003

BALDWIN SHELSTON WATERS

Attorneys for:

10 University of Wollongong and Massey University

ABSTRACT

The invention relates to a cross-linking monomer having the structure $Q-(L)_n-P-(L')_m-Q'$, where Q and Q' are polymerisable units, L and L' are linkers providing direct or indirect electronic communication between Q and P and between P and Q' , and P is an 5 electrofunctional unit, and also to polymers prepared from such monomers.

Q for example may be a heteroaromatic ring such as thiophene, furan and pyrrole. The electrofunctional group may be, for example, porphyrin, substituted porphyrin, phthalocyanine or substituted phthalocyanine. The invention also relates to an electrofunctional material including a base material and a cross-linked polymer such as 10 described.

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